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REVERSE OSMOSIS TREATMENT OF CONCENTRATED FERROUS IRON ACID MINE DRAINAGE

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Federal Water Quality Administration
Norton, West Virginia

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By

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ABSTRACT

A 4,000 gpd reverse osmosis unit was tested on a severely polluted ferrous iron acid mine discharge near Morgantown, West Virginia. The water recovery rate was limited to fifty percent due to membrane fouling problems. The role of ferrous iron fouling could not be identified because of a predominance of calcium sulfate precipitation on the membranes.

The feasibility of reverse osmosis treatment is doubtful for mine drainage having concentrations of acidity, iron, sulfate, and calcium as high as 5,000 mg/l, 2,300 mg/l, 10,000 mg/l and 525 mg/l, respectively, due to the membrane fouling problem, maximum recoveries of only 50 percent, and the non-potable quality of the product water.

Key Words: Reverse Osmosis, ferrous iron, acid mine drainage, membrane fouling, calcium sulfate precipitation.

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SUMMARY AND CONCLUSIONS

As part of Contract No. 14-12-525, the Federal Water Quality Administration and Gulf General Atomic, Inc. cooperated in a series of tests with a 4,000 gallon per day reverse osmosis unit to investigate its feasibility for treatment of a high ferrous iron acid mine drainage water. The water had the following characteristics: Ferrous iron = 1280 mg/l, total iron = 2300 mg/l, acidity = 5230 mg/l, calcium = 526 mg/l, sulfate = 10,900 mg/l, and pH = 2.24.

The tests, which were made near Morgantown, West Virginia, proved that reverse osmosis could successfully treat acid mine water with high acidity, iron, and sulfate concentrations at a maximum water recovery rate of 50 percent. This water probably represents the uppermost concentration of mine drainage pollutants that can be handled by reverse osmosis treatment.

Even though the rejections of the specific ions exceeded 97 percent, the product water quality was below potable standards and would require additional treatment before use.

The feasibility of reverse osmosis treatment of mine water of this quality is questionable due to the problems of disposing of the large volume of brine, frequent cleaning of membranes, and additional treating of the product water required before use.

An additional purpose of these tests was to evaluate membrane fouling by ferrous iron as has been reported by Rex-Chainbelt.[1] We were unable to evaluate the effects of ferrous iron at this site because of the calcium sulfate fouling problem.

RECOMMENDATIONS

As it was not possible to evaluate the ferrous iron fouling of the membranes from the tests conducted at the Morgantown site, it is recommended that additional tests be made at a site having a mine discharge with the following characteristics: pH = 2.7 - 3.0, acidity = 600, total iron = 200, ferrous iron = 125, and sulfates = 900.

In addition to evaluating ferrous iron fouling, the results from the recommended site would be comparable to data collected previously at the Federal Water Quality Administration's Norton Field Site since the water would have similar characteristics except for the ferrous iron. Also, at the lower concentration, the danger of calcium sulfate precipitation is less. Thus, the effects of ferrous iron fouling could be isolated and evaluated.

INTRODUCTION

Contract No. 14-12-525, between Gulf General Atomic, Inc. and the Federal Water Quality Administration, calls for a cooperative study of the treatment of acid mine drainage by reverse osmosis. Two types of water were to be treated during the study, i.e. ferric iron acid mine drainage and ferrous iron acid mine drainage. The first test was with ferric iron acid mine drainage at the FWQA Norton Field Site. With the assistance of Dean Charles T. Holland of the West Virginia University School of Mines, a high ferrous iron site was located. The site was the Indian Creek acid mine discharge located ten miles south of Morgantown, West Virginia, at the Arkwright Mine of Christopher Coal Company.

The test reverse osmosis unit was a Gulf General Atomic 4K (nominal 4,000 gpd product flow) unit using spiral wound modules. The entire 4K unit and support wiring was housed in an 8' x 20' metal building so that the entire system was portable. On site chemical analyses were also performed in this building. Acidity, ferrous iron, pH, and conductivity analyses were performed on site and the samples then acidified and returned to the Norton Laboratory for the remainder of the analyses. Dissolved oxygen (D.O.) determinations, which were made at the site, were unstable but in the range of 4.5 ppm. Attempts at using a modified Winkler Method on the brine were unsuccessful because of the ferrous iron concentration.

The flow diagram for the 4K unit and support facilities is shown in Figure 1.

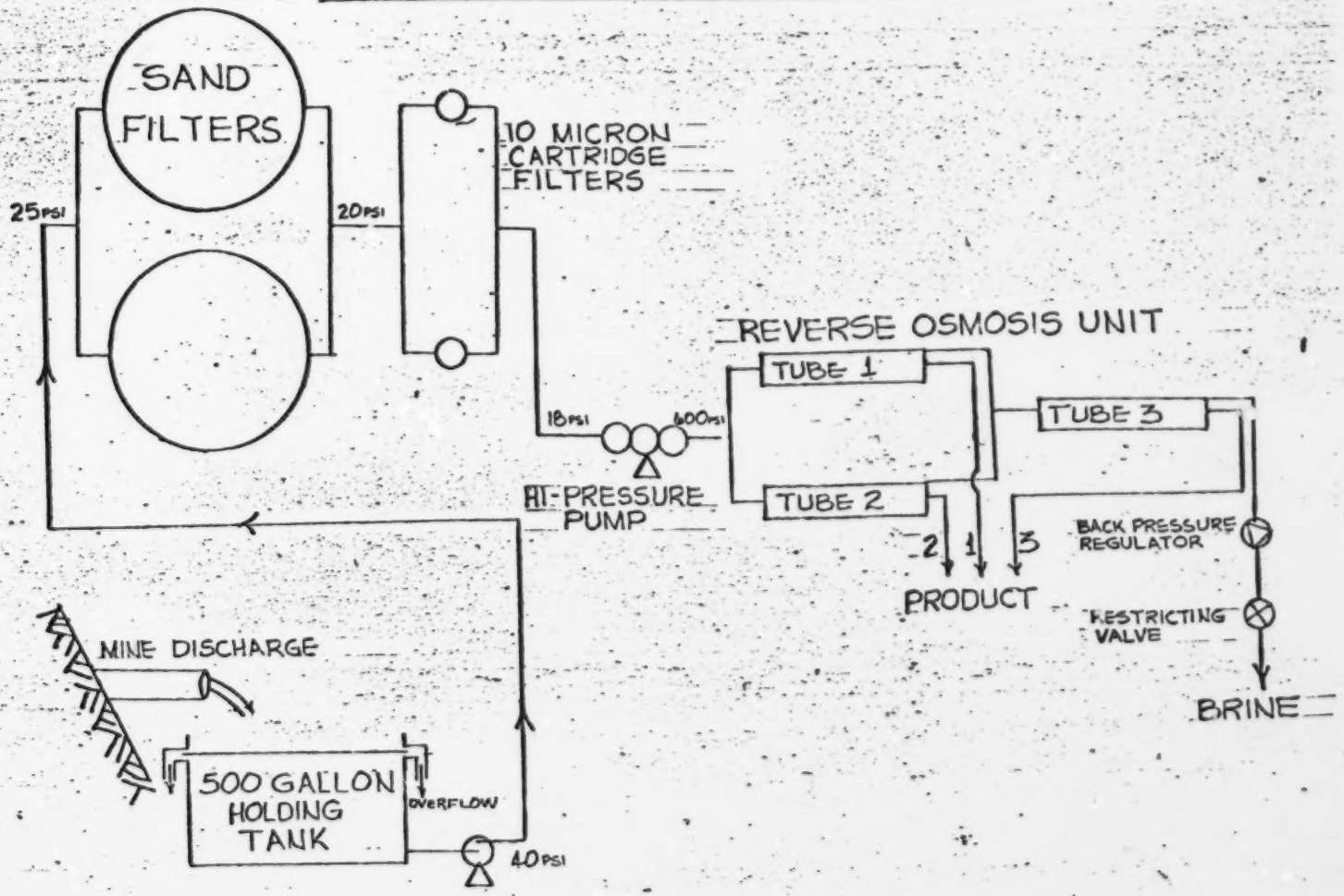
The 500 gallon holding tank was necessary as the mine water was pumped only intermittently from the borehole (on eight minutes, off five minutes). Pressured sand filters and 10 micron cartridge filters were used to remove any suspended solids from the feed water before the water entered the reverse osmosis unit. This was necessary as suspended solids can foul the reverse osmosis membranes.

The 4K unit utilized spiral wound modules which were three feet long, 3.75 inches in diameter, and contained 50 square feet of membrane. There were two effluents from the module, i.e., concentrated brine and product water. Typically, the brine from one module (or tube of modules) serves as the feed to the next module (or tube of modules) and is progressively dewatered in this manner. At this site, the brines from tubes 1 and 2 were combined to serve as the feed for tube 3. The entire 4K system contained approximately 450 square feet of membrane area.

Initially, tubes 1 and 2 contained standard flux, high selectivity modules and tube 3 contained high flux, intermediate selectivity modules. These modules had been in operation approximately 180 hours prior to this study. After the first test run, the modules were badly fouled and were replaced. The loading for the second test was: tube 1, new high flux modules; tube 2, new standard flux modules; and tube 3, used high flux modules.

FIGURE 1

FLOW DIAGRAM FOR 4K REVERSE OSMOSIS UNIT



Actual testing at this site began on May 13, 1970, and continued through May 26, 1970.

ANALYTICAL PROCEDURES

Acidity was determined according to the Salotto[2] method of adding hydrogen peroxide and titrating potentiometrically to a pH of 7.3 end point. Total iron, aluminum, calcium, and magnesium concentrations were determined by atomic adsorption spectrophotometry. Standard Methods[3] was used for the sulfate determination. A YSI* Model 51 D. O. meter was used for dissolved oxygen and was calibrated against an Azide Modified Winkler Method[3] run on distilled water. Attempts at Permangenate Modification[3] determination of D. O. were unsuccessful on the ferrous iron water. The pH was determined potentiometrically. Ferrous iron was determined by colorimetrically titrating potassium dichromate against a p-Diphenylamine sulfonic acid sodium salt indicator.[4]

RESULTS

The history of the test run is presented in Table I and the chemical analyses are reported in Table II.

The first run, lasting 45.7 hours, was begun at low pressure and 40 percent water recovery. The recovery was gradually increased by raising the pressure until 50 percent recovery was established. Unfortunately, data was available for only the first 27.8 hours. The differential pressure, which indicates rapid fouling, increased initially but levelled off after four hours of operation. However, the performance of the membrane, as illustrated by the water permeation coefficient 'A', showed a definite decreasing trend as shown in Table III. A decrease in the 'A' value of a membrane indicates that the membrane is passing less water. In this test, the large decrease in 'A' value was due to membrane fouling.

The second test was begun at 50 percent water recovery and lasted 66.1 hours, but data was available for only the first 46.4 hours. At the end of 66.1 hours, the unit was badly fouled by precipitation which occurred when a brass valve corroded and diminished the water supply to the unit, thus the unit was receiving only recirculated brine. As shown in Table III, the water flux decreased 21 percent in 46.4 hours of operation. The 'A' value for tube 3 (where the precipitation problems are most acute due to the higher concentration of ions) decreased 19 percent. This high decrease in tube 1 (loaded with new high flux modules) was difficult to explain,

*Mention of commercial products does not imply endorsement by the Federal Water Quality Administration.

Table I
4K Reverse Osmosis Operational History
Ferrous Iron Site, Morgantown, W. Va.

Date	Time	Elapsed Time	Pressure	Recovery	Product Flow gpm	Brine Flow gpm	ΔP (a) psi	Temp.	'A' (b)
RUN #1									
5/13/70	0	0	400	Unit started					
5/13/70	3.6	3.6	400	39.5%	2.30	3.52	9.9	68°F	1.896
5/13/70	4.1	4.1	500	47.0%	3.33	3.75	11.0	68°F	2.133
5/14/70	22.0	22.0	500	43.5%	2.86	3.70	11.0	64°F	1.967
5/14/70	27.8	27.8	600	49.1%	3.57	3.70	11.1	67°F	1.862
5/14/70	28.8	Power Failure							
5/15/70	45.7	Unit shut down - No feed pressure - Pump air lock Modules badly fouled Replacement modules installed (some used)							
5/21/70	0	0	400		2.50	4.00			
		Unit shut down for inspection of tubes 1&3 (high cond.)							
5/21/70	1.7	1.7	Probed tubes for leaky modules						
5/21/70	9.8	9.8	Shut down again for inspection Replaced modules and O-Rings						
5/21/70	21.7	21.7	Feed pump leaking, unit flushed with acidified product water Replaced pump and 3 more modules Restarted unit						
RUN #2									
5/22/70	22.7	0	400	41.6%	2.64	3.70	10.5	68.5°F.	2.226
5/22/70	23.8	1.1	600	52.5%	3.87	3.48	-	68°F	1.986
5/22/70	25.0	2.3	600	51.4%	3.84	3.64	11.1	68 F	1.973
5/23/70	40.5	17.8	600	50.0%	3.45	3.46	10.3	62°F	1.969
5/24/70	65.2	42.5	600	47.5%	3.23	3.57	11.3	64°F	1.778
5/24/70	69.1	46.4	600	46.7%	3.13	3.57	11.2	70°F	1.560
5/25/70	88.8	66.1	600				> 12.0		
5/25/70	89.3	Begin low pressure flush							
5/26/70	111.6	88.9	240	20.7%	1.05	4.00	No change	63°F	1.667
	111.7	Terminate testing							

(a) Pressure drop across unit = pressure in - pressure out
(b) 'A' - Water permeation coefficient (gallons/square feet membrane/minute/psi net pressure)$\times 10^{-5}$

Table II

Chemical Analyses - Reverse Osmosis Test Run
5/13 - 5/26/70 - Unit Recovery 50 Percent

Parameter	Feed	Brine	Product	Rejections*
pH	2.24	2.00	3.14	
Dissolved Oxygen	4.5	4.5	0	
Conductance	7040	11840	423	94.0%
Acidity as $CaCO_3$	5230	10050	148	97.2%
Calcium	526	933	9.6	98.2%
Magnesium	420	810	7.6	98.2%
Aluminum	317	598	5.0	98.4%
Sulfate	10920	20480	191	98.3%
Iron (Ferrous)	1280	2450	29	97.7%
Iron (Total)	2300	4460	39	98.3%
% Ferrous	48.9%	54.9%	74.3%	

$$\text{*Rejection} = \frac{\text{Feed Conc.} - \text{Product Conc.}}{\text{Feed Conc.}} \times 100$$

All units are mg/l except for conductance (micromhos) and pH.

Table III

'A' Values* and ΔP Values for Test Runs

Run No.	Elapsed Time	Tube 1 'A'**	Tube 2 'A'**	Tube 3 'A'**	Unit 'A'**	Unit Normalized*** Water Flux gal/ft^2/day
1	3.6	1.688	1.688	2.348	1.896	8.19 (12.29 @ 600 psi)
	22.0	1.707	1.772	2.887	1.967	11.33 (13.60 @ 600 psi)
	27.8	1.568	1.647	2.259	1.862	13.41
	DIFFERENT MODULES					
2	2.3	2.222	1.620	2.203	1.973	14.21
	17.8	1.856	1.764	2.370	1.969	14.18
	42.5	1.620	1.686	1.883	1.778	12.80
	46.4	1.450	1.542	1.774	1.560	11.23

		Tubes 1 & 2 ΔP (psi)	Tube 3 ΔP (psi)	Unit ΔP (psi)
1	3.6	3.4	6.7	9.9
	22.0	4.0	7.2	11.0
	27.8	4.3	7.1	11.1
2	2.3	4.0	7.5	11.1
	17.8	3.5	7.0	10.3
	42.5	3.5	8.0	11.3
	46.4	3.5	8.0	11.2

* 'A' is water permeation coefficient (gallons/ft^2 of membrane/min/psi)

** 'A' x 10^{-5}

*** Normalized to 77°F (from GGA G.E.F. Curve 9/25/67)[6]

Note: In 'A' calculations, the osmotic pressure of the product water was ignored. The osmotic pressure of the feed/brine average was assumed to equal 100 psi @ 10,000 micromhos specific conductance. The pressure differential across the membrane was assumed to equal the applied pressure.

especially since tube 2 was in parallel to tube 1 and was subject to the same condition. After termination of the test run, an explanation for the tube 1 'A' decrease was found. The brine seal on the last module of the tube had failed and allowed water to bypass the module. The module produced progressively less water until it became severely fouled by precipitates.

If the results from tube 1 are ignored and the flux declines between tubes 2 and 3 are compared, the decrease appears to be a concentration phenomena, as a much greater decrease is observed in tube 3 where the concentration is the greatest.

There was no significant increase in the differential pressure for the unit or for the individual tubes. This indicates that the rate of fouling is not too severe to prohibit operation on this water at the 50 percent recovery level. The rejections of the various ions by the membranes was relatively high (97+ percent on all multivalent ions). The rejection of ferrous iron was somewhat lower than the rejection of ferric iron as trivalent ions are better rejected than are divalent ions.

DISCUSSION

The chemical composition of the feed water at the Morgantown site was similar to that of the brine from the reverse osmosis unit at the Norton site (Table IV). Attempts to further treat the brine from the Norton test by reverse osmosis had revealed that calcium sulfate fouling occurred at 50 percent recovery. Therefore, it was not surprising that 50 percent recovery was the maximum attainable at Morgantown.

The two test runs, though short lived, were terminated by equipment and facility problems, rather than module or membrane failure. However, membrane fouling was evident. As previously predicted, 50 percent recovery was about the maximum recovery possible before $CaSO_4$ deposition would begin rapidly fouling the membranes.

The effects of fouling were easily seen during the study by the decrease in the 'A' value for the membranes. Unfortunately, the exact cause of the fouling is difficult to determine. All the evidence points to calcium sulfate deposition but the role of ferrous iron could not be determined. Fourteen of the modules used in this study were returned to Gulf General Atomic, Inc. for post mortem analysis. They will attempt to find the exact cause of fouling and will investigate methods for flux restoration and cleaning.

During the study, a sample of brine at 50 percent recovery was collected and a precipitate formed within an hour. This precipitate was analyzed and Sleigh[5] reported the composition, as shown in Table V, to be virtually $CaSO_4$. There were trace amounts of iron present.

Table IV

Norton Reverse Osmosis (Neutrolosis Test)
Chemical Analyses

Unit Recovery 91 percent (total recovery = 98.8 percent) 5/11 - 5/15/70

Parameter	Feed	Blended Feed	Brine	Product	Rejections*
pH	2.7	2.2	2.0	3.4	
Conductance	1,720	5,160	10,000	335	93.5%
Acidity as $CaCO_3$	657	2,677	6,030	130	95.1%
Calcium	100	473	1,127	3.0	99.4%
Magnesium	38	271	547	1.5	99.4%
Aluminum	38	187	405	1.1	99.4%
Sulfate	982	4,680	11,110	21	99.6%
Iron (Ferrous)	5**	-	-	-	-
Iron (Total)	117	516	1,210	1.6	99.7%
% Ferrous	4%				

$$\text{*Rejections} = \frac{\text{Blended Feed Concentration-Product Concentration}}{\text{Blended Feed Concentration}} \times 100$$

**Ferrous iron determinations not normally made on this water.
All units in mg/l except for conductance (micromhos) and pH.

Note: 'Neutrolosis' is a term applied to combination reverse osmosis and neutralization treatment of the raw water. The brine from the reverse osmosis unit is neutralized and the supernatant recycled into the feed. The only discharges from the neutrolosis process are product water and sludge.

Table V

Chemical Analysis of Brine Precipitate[4]

	Percent
CO_3	<0.5
Fe	0.70
Mg	0.5
*SO_4	63.0
*Ca	25.0
Al	<0.3
Clay and Silica	1.5
Other	8.5
	100.0

*Present in stoicheometric amounts found in $CaSO_4$

Sample: 5/23/70, 50 percent recovery.

A sample of the precipitate which lined the pressure vessel was analyzed and the results shown in Table VI. The composition of the in-unit precipitate is similar to the external brine precipitate of Table V.

The majority of the precipitation in the unit occurred during the last few hours before the runs were terminated. In both test runs, mechanical problems caused the recovery to soar to undetermined levels (probably greater than 90 percent) before the unit shut down and thus the brine was very concentrated and precipitation occurred. As calcium sulfate is the first salt to exceed solubility, it is expected that the precipitate would be largely calcium sulfate. The results in Table VI confirm this conclusion.

However, this predominance of $CaSO_4$ deposition may not be representative of what occurs during successful operation. The possibility of ferrous iron fouling cannot be ruled out nor can it be substantiated by these results.

Contrasting the salt rejections at Morgantown with those at Norton, the rejections at Norton are slightly higher in most cases. This difference in rejection rates is due to the high ionic concentration at Morgantown whose higher osmotic pressure results in less product flow while the salt flow remains essentially the same.

In conclusion, the unit performed satisfactorily under very adverse water conditions. However, it does not not appear that reverse osmosis would be a feasible method for treatment of water of this quality, based upon these problems: membrane fouling; limited recovery (fifty percent) which requires disposal of an equal volume of brine for each gallon of water reclaimed; and low quality product water. Further treatment of the product water would be necessary to bring it up to potable standards. This additional treatment could be accomplished by treating the product water with another reverse osmosis unit and then polishing the effluent with lime to increase the pH.

Table VI

Chemical Analysis of Solids in Unit After Shutdown[4]

	Percent
CO_3	<1.
Fe	<0.3
Mg	1.6
SO_4	60.8
Ca	21.7

Date: 5/17/70, Tube 3 Pressure Vessel

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